Nonanthropogenic Standard Selection: Madison River, Madison County, Montana

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ACRONYMS

ARM	Administrative Rules of Montana
cfs	Cubic feet per day
DEQ	Department of Environmental Quality
DON	Demonstration of Nonathropogenic
EPA	Environmental Protection Agency
HUC	Hydrologic Unit Code
ICIS	Integrated Compliance Information System
kg/day	Kilograms per day
MCA	Montana Code Annotated
ML	Mass Load
NAS	Nonanthropogenic Arsenic Standard
QAPP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan
TMDL	Total Maximum Daily Load
ug/L	microgram per liter
USGS	United States Geological Survey
WQPB	Water Quality Planning Bureau
WQSM	Water Quality Standards and Modeling Section
WWTP	Waste Water Treatment Plant
YNP	Yellowstone National Park

1.0 INTRODUCTION

This document presents the methods and results for arsenic nonanthropogenic standard (NAS) selection for the Madison River. NAS selection is a process used to identify appropriate water quality standards in situations where a waterbody's levels of a pollutant are elevated due to natural (non-human) sources. The project includes the portion of the Madison River watershed from the Yellowstone National Park (YNP) boundary to the mouth of the Madison River near Three Forks. The Water Quality Standards and Modeling Section (WQSM) of the Montana Department of Environmental Quality (DEQ) Water Quality Division has completed this document.

1.1 PURPOSE

Although water quality standards are almost always expressed as a unique concentration value, water quality is not simply a static number. Water quality is almost always a distribution of concentration values which, over a long period of time, typically appears static, but in the short term, can be quite variable. The variability is a result of seasonal changes and inter-annual fluctuations. The Madison River below Ennis Lake (**Figure 1-1**) serves as an excellent example of the variability of arsenic concentrations over time and the inherent difficulty in picking a unique concentration value to represent the "natural" condition of the water body. The purpose of a nonanthropogenic water quality standard is to protect the existing uses of the water body and to protect the long-term nonanthropogenic distribution of values, to the extent possible. While it would be nearly impossible to preserve the exact distribution of values, choosing an appropriate criterion within the distribution can help ensure that the important part of the distribution necessary to maintain existing uses and conditions is protected.

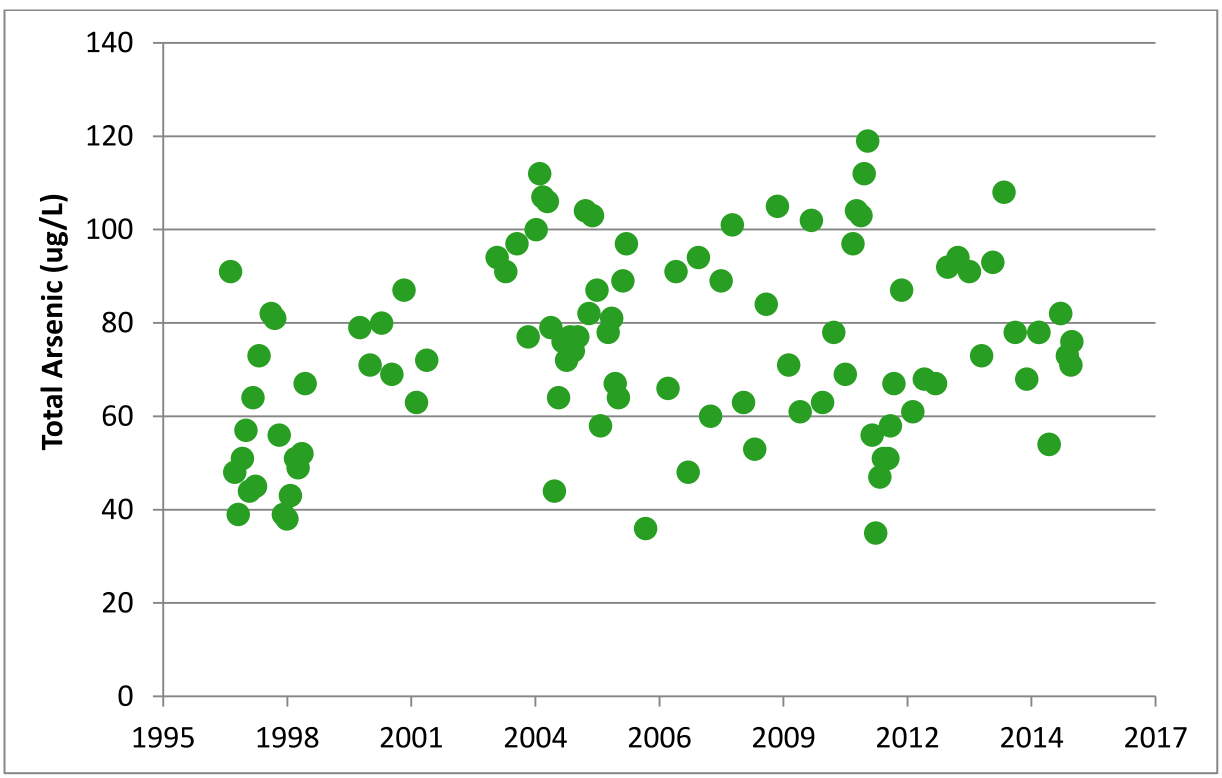

Figure 1-1. Concentration Patterns for the Madison River below Ennis Lake

1.2 Supporting Documents

The "Demonstration of Nonanthropogenic" (DON) document summarizes the methods and results for the demonstration of nonanthropogenic arsenic for the Madison River and will be referenced throughout this document (DEQ, 2017). A scientifically defensible DON is a first step in the process of developing standards based on a nonanthropogenic condition. The NAS is based on the methods and results detailed in the DON (DEQ, 2017).

The quality assurance descriptions for field data collection, data compilation and modeling described in this document were provided in the Department of Environmental Quality (DEQ) Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plans (SAP) (DEQ, 2015a, 2015b, 2016b). Full citations are located in the reference section of this document.

1.3 Background

In YNP, there are over 10,000 thermal features including more than 300 geysers (YNP, 2015). The Firehole and Gibbon Rivers join in the park to form the Madison River. The Madison River eventually joins the Jefferson and Gallatin rivers near Three Forks, Montana to form the headwaters of the Missouri River. A recent DEQ Madison River/Upper Missouri Water Quality Assessment and TMDL project reported arsenic concentrations of samples collected from the Madison River above the Montana human health standard of 10 µg/L (DEQ, 2016a, 2012). Per 2015 Senate Bill 325, codified as Montana Code Annotated (MCA) 75-5-222, DEQ may not apply a water quality standard to a water body that has nonanthropogenic concentration greater than the standard (75-5-222, MCA). In this case, since the human health-based standard of 10 µg As/L is below the nonanthropogenic condition (see DEQ 2017), then the standard would be set at the natural arsenic condition of the water body.

DEQ WQSM section conducted an investigation to characterize the level of nonanthropogenic arsenic concentrations in the Upper Missouri Basin. The specific objectives of the WQSM investigation are described in the project QAPP (DEQ, 2015a) and SAPs (DEQ, 2015b, 2016b). The results applicable to the NAS are described in this document.

1.4 Hydrologic Region

The hydrologic region of interest is the Madison River watershed from the YNP Boundary to the mouth. Hydrologic basins can be classified using the United States Geological Survey (USGS) Hydrologic Unit Code (HUC) system. This system assigns a specific two-digit number to 21 major watersheds throughout the United States, and then uses progressively longer numbers to divide the basin into smaller sub-basins. An example of the progression from HUC2 to HUC12 for the Madison River watershed is listed below. The Madison River HUC8 code is 10020007 and defines the entire Madison River from its headwaters in YNP to the mouth of the Madison River near Three Forks. Smaller geographic regions within this HUC8 were recognized for modeling purposes. For example, there are 64 HUC12s within the Madison Basin (**Figure 1-2**).

- HUC2 (10): Missouri River (entire watershed)
- HUC4 (1002): Missouri Headwaters (above Three Forks)
- HUC6 (100200): Missouri Headwaters (same as HUC4 in this particular case)
- HUC8 (10020007): Madison River (entire watershed)

- HUC10 (1002000702): Headwaters Madison River (near West Yellowstone)
- HUC12 (100200070203): Upper South Fork Madison River

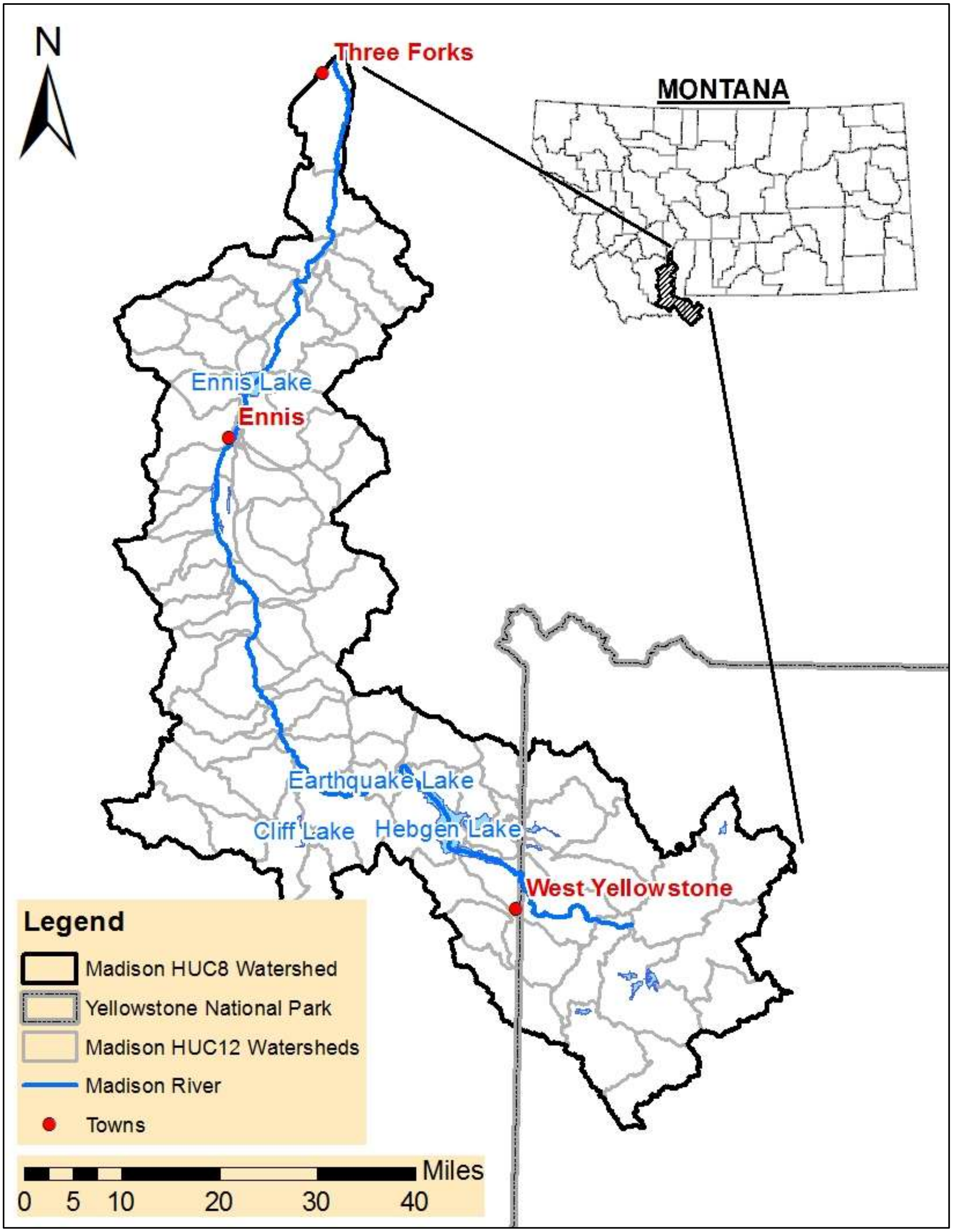

Figure 1-2. Location of Project Sub-basins

The Madison River and associated tributaries are divided into three hydrologic sections for standards development. The sections are based on the regional hydrologic divisions caused by the dam infrastructure and USGS gaging locations, and are shown in **Figure 1-3**. The three hydrologic sections are:

- YNP Boundary to below Hebgen Lake
- Below Hebgen Lake to below Ennis Lake
- Below Ennis Lake to the mouth of the Madison River

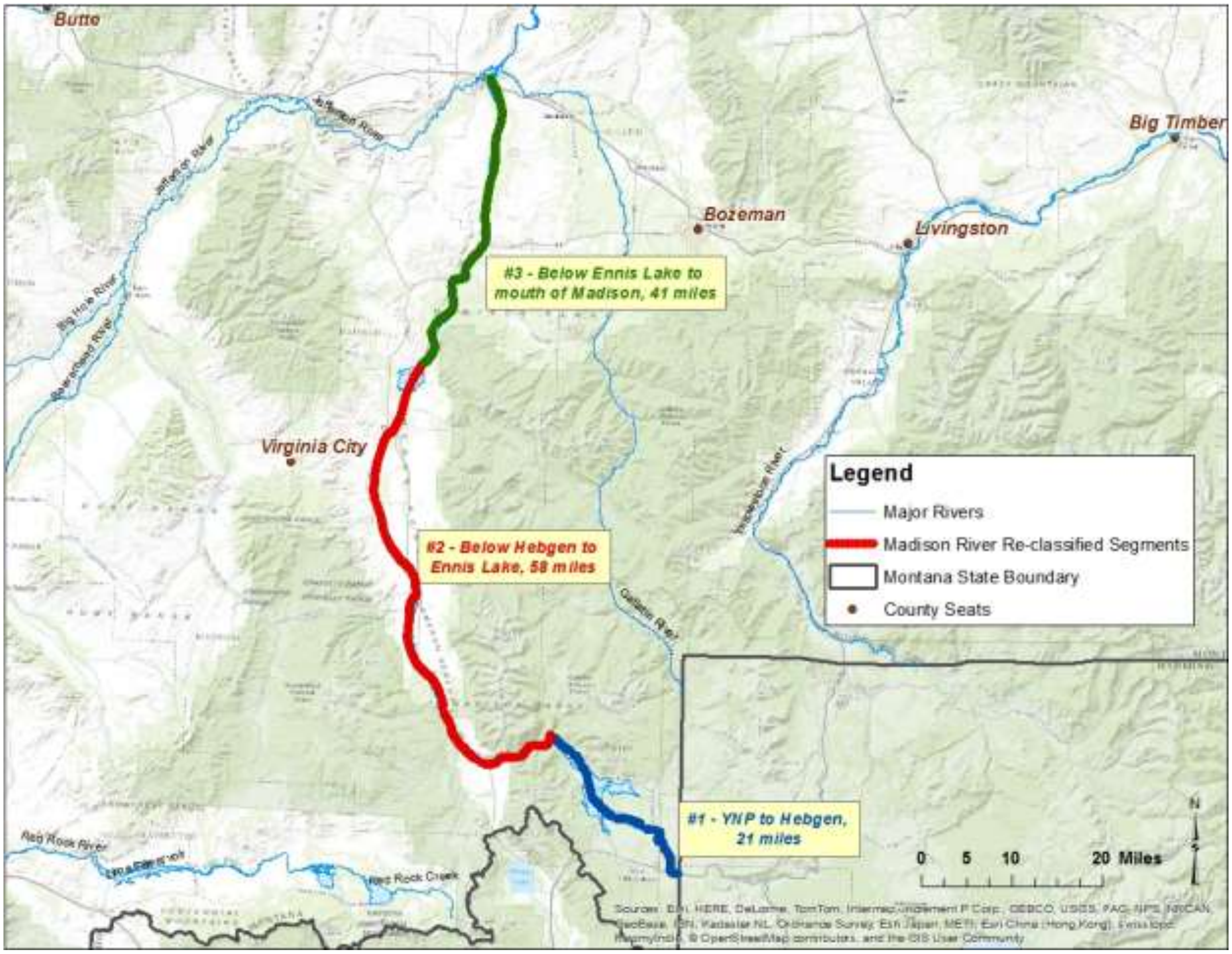

Figure 1-3. Hydrologic Sections of the Madison River

The arsenic loads and concentrations become homogenized within the reservoirs as a result of the detention time within the structure. Each segment has a vastly different median concentration. As the river leaves YNP, arsenic concentrations are high from natural geothermal sources. Tributaries dilute these high arsenic concentrations resulting in successively lower concentrations downstream from YNP in the Madison River.

2.0 METHODS

The steps associated with NAS Selection are listed below and summarized in **Figure 2-1**. These steps will be discussed in the succeeding sub-sections.

- Demonstration of Nonanthropogenic (DON)
- Existing or Potential Dischargers
- Dilution Test
- Seasonality Determination
- Standard Selection

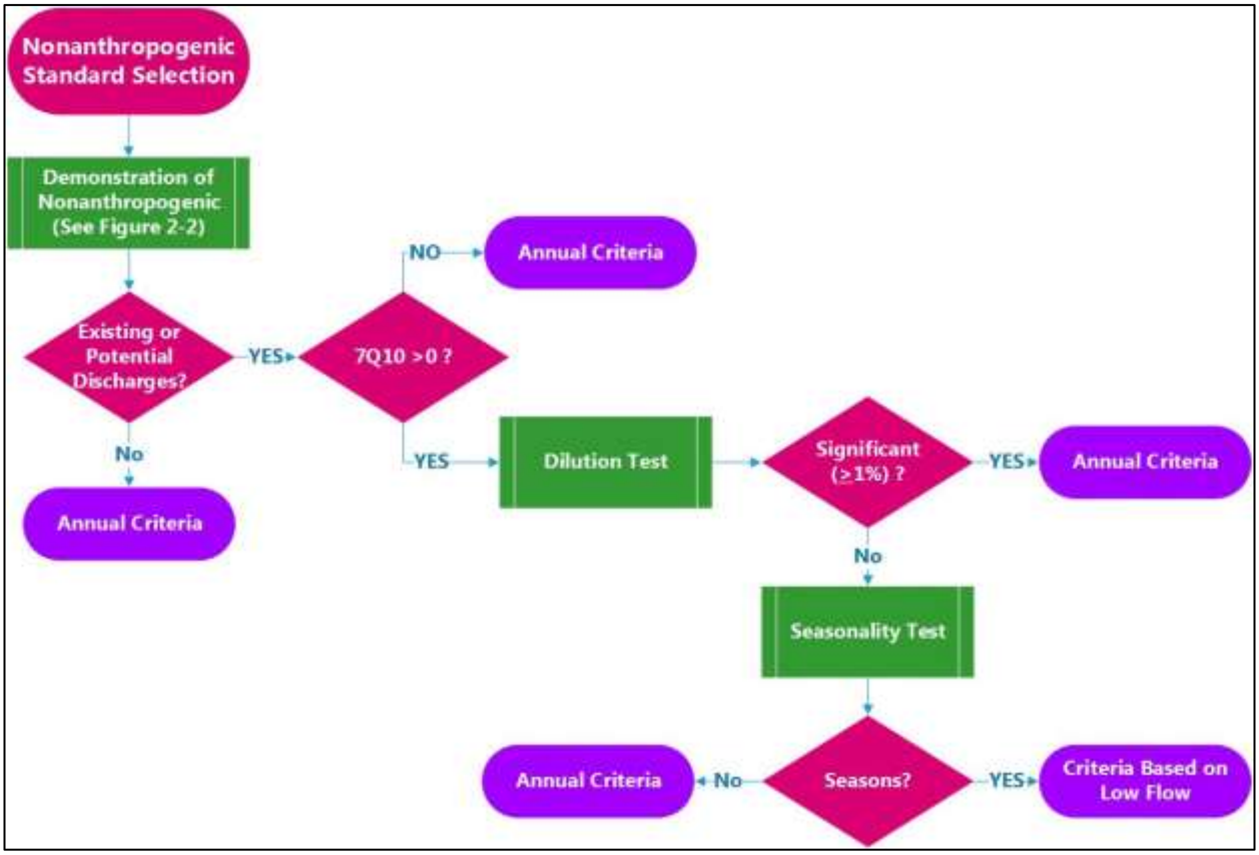

Figure 2-1. Nonanthropogenic Standard Selection (NAS) Flow Chart

2.1 DEMONSTRATION OF NONANTHROPOGENIC (DON)

A scientifically defensible DON is the first step in the process of developing criteria based on a nonanthropogenic condition. The process for calculating nonanthropogenic arsenic loads for the Madison River Basin is shown in **Figure 2-2**. The DON concludes with the median nonanthropogenic arsenic load condition and is tabulated in **Table 3-1** (DEQ, 2017).

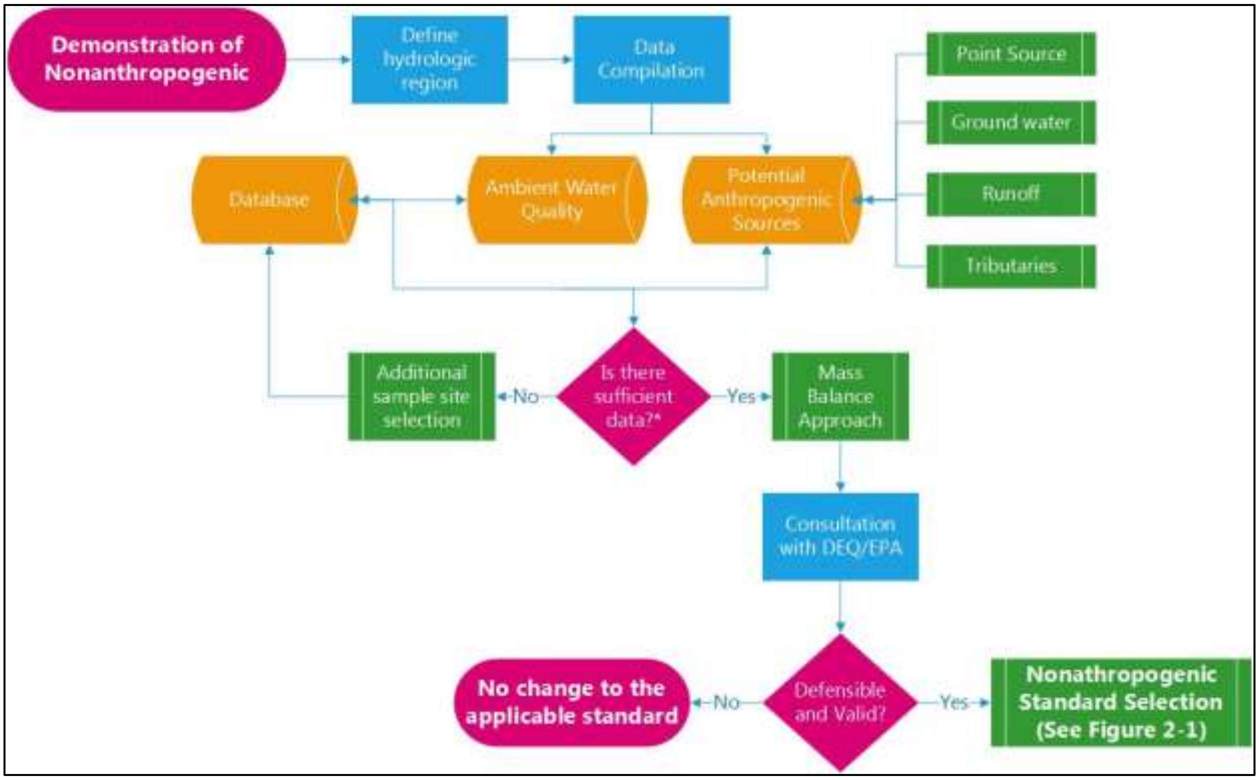

Figure 2-2. Demonstration of Nonanthropogenic Process

2.2 Potential or Existing Discharges

As shown in **Figure 2-1**, after the DON is completed and determined valid, the presence of discharges (or planned discharges) is determined. Permitted discharges include major facilities legally and actively discharging into the project waterbodies. The arsenic concentration data is extracted from the EPA Integrated Compliance Information System (ICIS) database. Additional research should be performed to determine if there are any other discharges from other point sources. Other potential sources may include active or inactive mining operations, remediation sites, leaky underground storage sites, or hazardous waste sites. These potential point sources are discussed in detail in the DON (DEQ, 2017).

Current or future discharges have the potential to shift the nonanthropogenic arsenic distribution of the water body in a manner inconsistent with the protection of beneficial uses. Arsenic concentrations in Montana are higher during low flow conditions compared to higher flow conditions. Therefore, setting a criterion based on year-round arsenic concentrations is more conservative than setting a criterion based on low-flow arsenic concentrations. The more conservative approach will be selected if there are no dischargers in a reach. If there are any future dischargers in the reach some day, the new discharger will be held to the more conservative criterion, and any discharges may be further limited because they will have to provide for attainment and maintenance of downstream water quality standards (see proposed new rule, draft Circular 14). This concept is further explained in the next section.

2.3 Dilution Test

The dilution test estimates if current or future discharges have the potential to shift the nonanthropogenic arsenic distribution of the water body in a manner inconsistent with the protection of beneficial uses.

The nonanthropogenic distribution of arsenic concentrations in a large river is much better protected against potential changes caused by permitted arsenic discharges than is the arsenic distribution of a smaller stream with lower flows. In order to assess this volume-based sensitivity, a dilution test is carried out by comparing a water body's 7Q10 flow (the lowest average 7-day low flow that occurs once every 10 years on average) to existing and potential discharge volumes. The 7Q10 for many Montana waterbodies can be found in Appendix E of the USGS publication, Montana Stream Stats (USGS, 2015). Use of the 7Q10 for the dilution test is meant to evaluate the potential for a shift in the distribution of arsenic concentration values during some of the lowest expected flows (i.e. in the worst-case scenario for dilution purposes).

If the 7Q10 value of a stream is zero cfs, then current or future discharges to that stream are significant and an annual standard based on the median monthly nonanthropogenic concentrations would be applied (**Figure 2-1**). If the 7Q10 is greater than 0, then a ratio of the cumulative point sources' discharge volumes (existing and any planned discharges) to 7Q10 flow is calculated. If the ratio is greater than or equal to 1%, the collective discharge is considered significant and an annual standard based on the median monthly nonanthropogenic concentrations would be applied. If the ratio is less than 1%, then a seasonality determination is required. 1% was chosen because there is precedence for using 1% dilution to indicate that sufficient dilution will occur. The Montana Pollutant Discharge Elimination System permitting program uses a cutoff of 1% dilution to indicate whether the discharge is small enough in relation to the receiving water to allow a standard mixing zone granting 100% of the 7Q10 for dilution calculations (ARM 17.30.416). The seasonality determination is described in detail in **Section 2.4**. The dilution test qualifications are summarized in **Table 2-1**.

Table 2-1. Dilution Test for NAS Selection

Case	7Q10 (cfs)	Point Source Discharge Volume % of 7Q10	Standard Selection or Action
1	0	N/A	Select Annual Standard
2	> 0	0	Select Annual Standard
3	> 0	$\geq$ 1%	Select Annual Standard
4	> 0	< 1%	Perform Seasonality Determination

2.4 Seasonality Determination

If the dilution test demonstrates that a seasonality determination is appropriate (**Table 2-1**), the modeled nonanthropogenic arsenic concentration for the water body is analyzed for variability under high flow versus low flow conditions. This determines if the annual standard will be based on the median concentrations of all months or just the low flow months. This will be done per the method identified in Suplee (2007) and summarized in this section.

The USGS daily flow data and the median monthly arsenic concentrations calculated from the median of the daily flow data are used in the seasonality determination. First, high flow and low flow months are determined. In order to do this, at least five years of continuous flow data are necessary (this will normally be drawn from a USGS gaging station or stations within the reach). The recorded flows for each day of the year for the entire period of record are averaged and plotted on a flow duration hydrograph. The runoff period is then bracketed by determining the two points of inflection (where runoff and begins and ends) and rounding to the nearest end-of-month or mid-month date. The runoff period represents the high flow months, and the rest of the year represents the low flow months. An example of the daily mean flow hydrograph for the Madison River at West Yellowstone is shown in **Figure 2-3**. The high flow period is identified as starting and ending at the two inflection points on each side of the flow peak (127 and 205 days).

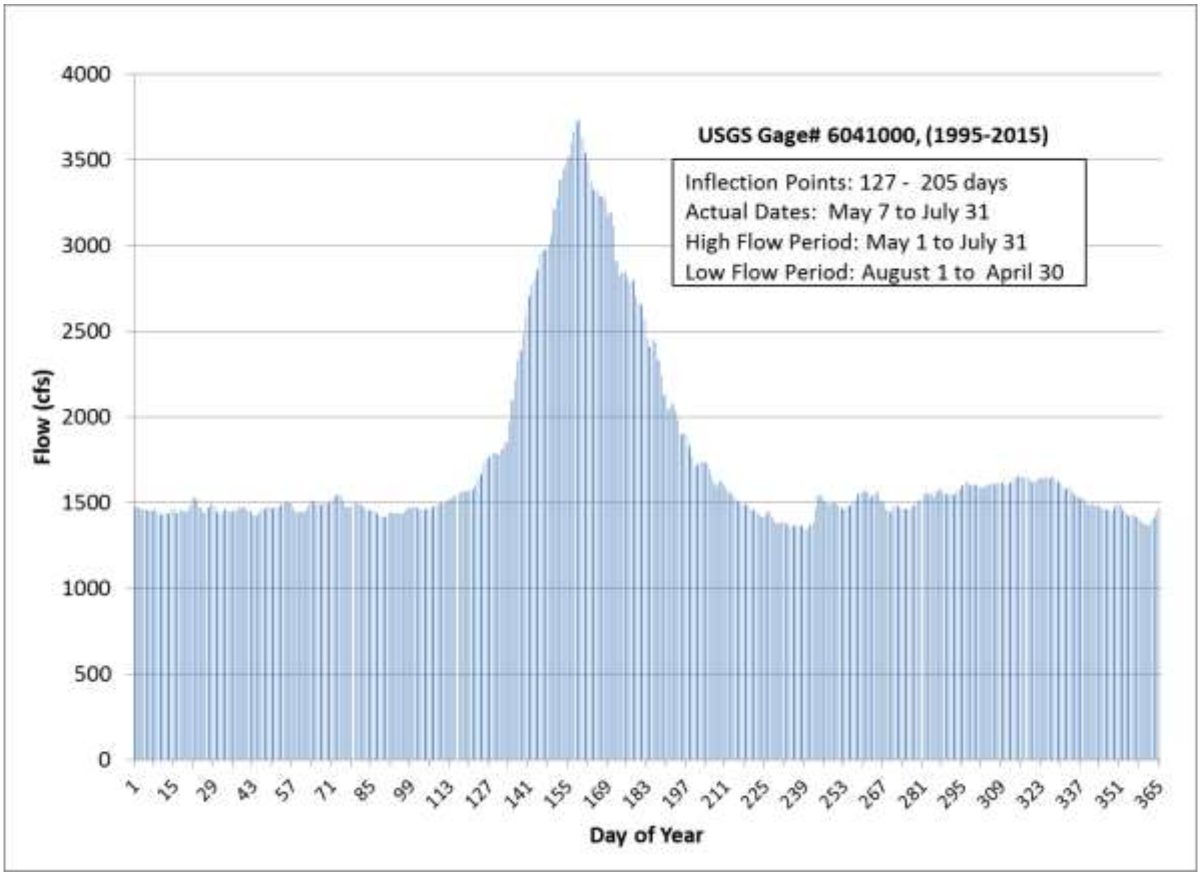

Figure 2-3. Example Daily Mean Flow Duration Hydrograph for Madison River at West Yellowstone

If data for comparison are limited, DEQ may model and use ambient arsenic data to test seasonality. For example, if there are only 2 low flow months and 10 high flow months, using the monthly nonanthropogenic concentrations would only provide an n=2 for the low flow months. This is not enough data to complete a valid statistical test. Under these circumstances, a larger dataset is necessary to determine seasonality. The ambient concentration data set can be used for the analysis if the nonanthropogenic load is at least 95% of the ambient condition. This allows for inherent error that is associated with mass balance calculations and the resulting nonanthropogenic loads. The unaccounted arsenic load at the mouth of the Madison River was approximately 4% of the total arsenic load and is either calculation error or an unaccounted load from groundwater contribution (DEQ, 2017). Either way, far and away the vast majority of the arsenic load is natural and lends itself to this analysis.

After determining the high flow and low flow months, the model-derived monthly arsenic concentrations from these two time periods are tested for a significant difference (95% confidence, α= .05) using the Mann-Whitney test. The Mann-Whitney test is a nonparametric hypothesis test to determine whether two populations have the same population median.

The hypotheses are:

H_0: $x_1 = x_2$ versus H_1: $x_1 \neq x_2$, where x is the population median

The test does not require the data to come from normally distributed populations but the sample sets should have similar shape and be independent of each other. The test uses the ranks of the sample data, instead of their specific values, to detect statistical significance. The selected α (significance level) is the maximum acceptable level of risk for rejecting a true null hypothesis (H_0). The test calculates a p-value (between 0 and 1) and determines the appropriateness of rejecting H_0 in the hypothesis test. The p-value must be less than the selected α (0.05) to reject H_0 in favor of the alternate hypothesis (H_1), thus concluding that the two populations are different. Alternately, a test that results in a p-value greater than α does not support the hypothesis that there is a difference between the population medians.

If the median arsenic concentrations for the high and low flow seasons are significantly different per the Mann-Whitney test, then seasonal criteria will be calculated and one annual standard will be applied based on the median monthly concentrations of the low flow season. Alternately, if the median arsenic concentrations for the high and low flow seasons are not significantly different per the Mann-Whitney test, then one annual standard based on the median monthly arsenic concentrations is applied.

Overall, this approach protects water bodies when they are most vulnerable to change during low flow conditions or if point source discharges make up a significant portion of the flow. It also allows a slightly higher standard if the water body's arsenic concentrations are protected from changes due to higher flows and therefore higher dilution.

2.4 Standard Selection

As mentioned in the previous section, the water quality standard, whether seasonal or annual, is based on the 50th percentile (median) of the nonanthropogenic distribution. If the nonanthropogenic condition was determined via a loading analysis, the standard will be calculated based on the long-term median flow for the designated time period. This approach establishes the water quality standard at a value that should be protective locally (i.e., largely representative of the nonanthropogenic condition) even if relatively large discharges were ultimately allowed that could move in-stream water quality concentrations nearer to the established standard. In other words, distributions of concentration data, if there are many dischargers and little dilution, will always change; in these cases, the central tendency will move towards the water quality criterion concentration (which would be equal to the 50th percentile), and the 50th percentile is about the best representation of the central tendency of the nonanthropogenic distribution of the data points.

A standard calculated based on ambient concentrations is less complicated than a standard calculated from a nonanthropogenic condition. For instance, in order to establish a standard based on ambient condition, a statistically valid number of concentration data points are collected, representing seasonal and annual fluctuations and a median concentration is calculated from this data to represent an annual or seasonal standard. There are many more steps when the standard is developed from the nonanthropogenic condition.

The first step in selecting the NAS is to calculate the nonanthropogenic condition as outlined in **Figure 2-2** and defined in the DON (DEQ, 2017). The DON not only demonstrates that the source of arsenic is mainly nonanthropogenic, but also establishes the monthly nonanthropogenic arsenic mass load. Standards are set as concentrations; therefore, the nonanthropogenic arsenic mass load must be converted to a concentration. A mass load is converted to a concentration using a flow volume, as defined in the following equation:

EQUATION 1: $C = ML/(Q \times T \times cf)$

Where,

- C – Concentration (µg/L or mg/L)
- ML – Mass Load (pounds or kilograms per unit of time)
- Q – Flow of water at a point (cubic feet per second, cfs)
- T – unit of time (season, month, or year)
- cf – conversion factor for mass load calculation (variable depending on units of individual terms)

While the 7Q10 flow is used to determine the worst case scenario in the dilution test, the median flow volume is used for calculating the arsenic standard. The median flow volume corresponds to a mid-level arsenic concentration rather than a very high arsenic concentration, and the intent is to select the central tendency for the standard rather than an outlier. If applicable to the stream body, the median monthly flow volumes can be calculated from USGS gage data as described in **Section 2.2**. However, if there is no USGS gage or other type of gage, the median flow rate is based on a statistically valid data set. The process of collecting a statistically valid data set for a nonanthropogenic condition is summarized in **Section 3.0** of the DON (DEQ, 2017).

3.0 Results

3.1 Demonstration of Nonanthropogenic

The Madison River will be presented as a specific example of the process described in **Section 2.0**. For the Madison River segments, the modeled monthly and annual median anthropogenic arsenic loads are tabulated in **Table 3-1**. Additional detail can be found in the DON (DEQ, 2017).

Table 3-1. Median Nonanthropogenic Loads for Madison River

Month	YNP to Below Hebgen	Below Hebgen to Ennis Lake	Below Ennis Lake to Mouth
Monthly (kg/month)			
October	7,454	7,637	7,030
November	7,462	8,518	7,487
December	8,116	10,324	8,558
January	8,477	11,666	9,439
February	7,909	10,467	8,955
March	8,891	10,813	10,335
April	8,711	10,241	9,211
May	10,591	10,279	11,173
June	8,904	9,619	12,452
July	7,773	7,993	8,163
August	7,259	7,331	6,653
September	7,047	7,129	6,272
Annual (kg/year)			
Annual	98,594	112,017	105,729

3.2 Dilution Test

As described in **Section 2.2**, a dilution test is carried out by comparing a water body's 7Q10 flow to existing and potential discharge volumes. The list of permitted discharges, facility, receiving body, maximum facility discharge and maximum facility concentration are shown in **Table 3-2**.

Table 3-2. Permitted Discharges

MPDES No.	Facility	Receiving Body	Maximum Flow (cfs)	Max Concentration (µg/L)
MTG130008	USFWS-ENNIS NAT FISH HATCHERY*	Madison below Hebgen	30	29
MT0030732	ENNIS WWTP	Madison below Hebgen	0.34	11
MT0000264	THREE FORKS DOMESTIC WWTP	Madison below Ennis Lake	1.02	34

*No arsenic limits. Flow volume and arsenic concentration of Blaine Spring Creek below Fish Hatchery Weir.

The maximum discharge was used in this analysis to illustrate a worst case scenario or the maximum discharge quantity for the facilities history. There were no other potential discharges identified for the Madison River. Please refer to the DON for additional discussions on point sources (DEQ, 2017). There were no potential discharges identified for the Madison River from YNP Boundary to below Hebgen Lake, two potential discharges (Ennis Fish Hatchery and Ennis Waste Water Treatment Plant (WWTP)) for the Madison below Hebgen Lake to Madison below Ennis Lake, and one discharge (Three Forks WWTP) below Ennis Lake to the Mouth. The sum of these discharges, the river's 7Q10, and the results of the dilution test are shown in **Table 3-3**.

Table 3-3. Results of Madison River Dilution Test

Station	USGS Gage Number	7Q10 (cfs)*	Max Permitted Flow (cfs)	Dilution Test (Max Flow/7Q10)	Conclusions
Madison YNP to Below Hebgen	06037500	304	0	0.0%	Annual Criteria
Madison below Hebgen to Below Ennis Lake	06038500	400	30.3	7.6%	Annual Criteria
Madison below Ennis Lake to Mouth	06041000	731	1.02	0.1%	Use Seasonal Determination

*7Q10 was obtained from USGS stream stats (USGS, 2015). The stream stat for the USGS gage below Hebgen Lake is very low when compared to other Madison River stations. This error in the calculation resulted from dam management prior to 1984. The 7Q10 for the Madison at Kirby Ranch (6038800) was used in place of the Madison below Hebgen Lake.

For all three stretches of the Madison River, the 7Q10 is greater than 0 and the ratio of the cumulative point sources' discharge volumes (existing and any planned discharges) to 7Q10 flow is calculated (**Table 3-3**). There are no permitted or potential discharges for the Madison River from YNP to below Hebgen Lake. Per **Table 2-1**, the standard would be one annual criteria based on median monthly nonanthropogenic concentrations. The Madison below Hebgen Lake has a dilution ratio greater than 1%; therefore, potential anthropogenic discharge is considered significant and one annual standard is applied and is based on the median monthly nonanthropogenic concentrations. The Madison River below Ennis Lake to the mouth has a dilution ratio less than 1% and requires a seasonality determination for NAS selection. The seasonality determination is described in **Section 3.3**.

3.3 Seasonality Determination

Only the lower segment of the Madison River below Ennis Lake to the Mouth of the Madison River requires a seasonality test for NAS development. Twenty years of daily flow data for the Madison River below Ennis Lake (USGS gage #06041000) is averaged and plotted on a hydrograph (**Figure 2-3**). The runoff period is bracketed by the two points of greatest inflection and rounded to the nearest end-of-month. The runoff period, May 1 to July 31, represents the high flow months, and August 1 to April 30 represents the low flow period.

The model-derived monthly anthropogenic arsenic concentrations from the high and low flow periods are tested for significant differences (95% confidence, or α= .05) using the Mann-Whitney test. The median monthly concentrations were calculated from the modeled nonanthropogenic arsenic load (**Table 3-1**) using **Equation 1** and the methodology described in **Section 2.4**. The model derived median nonanthropogenic loads, flow rates, and resulting concentrations are shown in **Table 3-4**.

Table 3-4. Madison River Below Ennis Lake: Model Derived Median Monthly Nonanthropogenic Arsenic Loads, Flow Rates, and Concentrations.

Month*	Median Nonanthropogenic Arsenic Load (kg/month)	Median Flow Rate (cfs)	Median Nonanthropogenic Arsenic Concentration (µg/L)
October	7,030	1,390	68
November	7,487	1,460	69
December	8,558	1,390	83
January	9,439	1,460	87
February	8,955	1,465	82
March	10,335	1,450	96
April	9,211	1,370	90
May	11,173	1,880	80
June	12,452	2,660	63
July	8,163	1,630	67
August	6,653	1,330	67
September	6,272	1,300	65

******High Flow Period in Blue and the Low Flow Period in Red.*

The results of the Mann-Whitney test showed a p-value (0.2) greater than the chosen alpha (.05) concluding that the median arsenic concentrations for the high and low flow seasons are not significantly different. Therefore, for the Madison River below Ennis to Three Forks, the standard will be one annual criterion based on the median monthly nonanthropogenic concentrations for the entire year.

3.4 Criteria Selection

The modeled loads, flow rates, and resulting median monthly nonanthropogenic concentrations for Madison below Ennis are presented in **Table 3-4**. The median monthly nonanthropogenic concentration results for the two Madison River segments from YNP to below Ennis Lake are shown in **Table 3-5**. The monthly median anthropogenic arsenic concentration is calculated from the median anthropogenic arsenic load and the median flow rate using **Equation 1** (**Section 2.4**).

Table 3-5. Madison River From YNP Boundary to Below Ennis Lake: Model Derived Median Monthly Nonanthropogenic Arsenic Loads, Flow Rates, and Concentrations

Month	Median Nonanthropogenic Arsenic Load (kg/month)	Median Flow Rate (cfs)	Median Nonanthropogenic Arsenic Concentration (µg/L)
Madison River YNP to Below Hebgen Lake			
October	7,454	418	240
November	7,462	417	240
December	8,116	403	271
January	8,477	400	285
February	7,909	394	270

March	8,891	406	294
April	8,711	489	239
May	10,591	791	180
June	8,904	686	174
July	7,773	444	235
August	7,259	411	237
September	7,047	405	234
Madison River Below Hebgen Lake to Above Ennis Lake			
October	7,637	896	115
November	8,518	888	129
December	10,324	952	146
January	11,666	962	163
February	10,467	911	154
March	10,813	928	157
April	10,241	942	146
May	10,279	1,030	134
June	9,619	1,115	116
July	7,993	1,030	104
August	7,331	990	100
September	7,129	944	101

For all Madison River segments, the selected NAS is one annual standard based on the median value of all monthly modeled data. The NAS is presented in **Table 3-6**.

Table 3-6. Madison River Segments and Selected NAS

Madison River Hydrologic Segments	Type of Standard	NAS (µg/L)
YNP to below Hebgen Lake	Annual	240
Below Hebgen Lake to below Ennis Lake	Annual	132
Below Ennis Lake to the mouth of the Madison River	Annual	75

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